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Development of CZTSSe Thin Film Solar Cells with Inclusions of Selenium in the Precursor Stack

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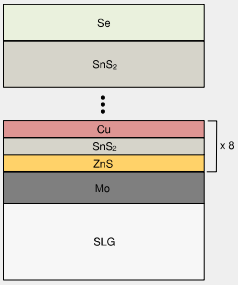
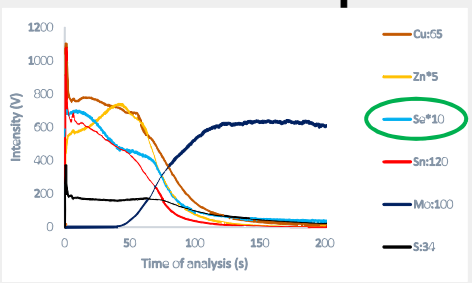
Abstract

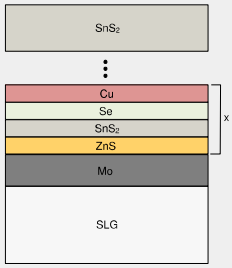
$Cu_2ZnSn(S_xSe_{1-x})$ (CZTSSe) solar cells were produced by sputtering of a precursor stack, where the element Se was thermally evaporated onto the precursors in two different configurations, followed by annealing in H_2S using an RTP furnace. The absorbers produced exhibited blisters. The S/(S+Se) profile in each configuration and blister formation investigations in CZTS are presented.

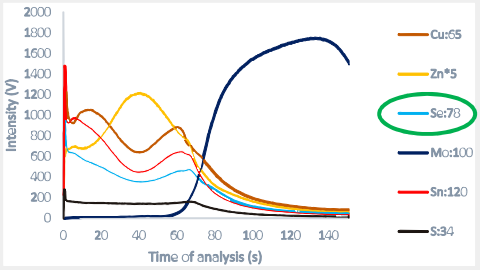
Composition Grading





Pulsed rf-GD-TOFMS analysis of the absorbers





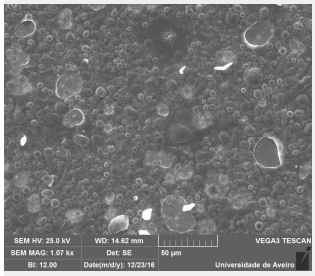
Se on top of precursors

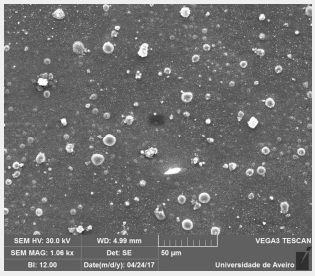
The composition profile reveals that there is a vertical gradient of Se, while the S profile remains nearly constant. This is consistent with a profile resulting from diffusion of Se from the surface into the absorber during annealing. However, the grading was low, with the S/(S+Se) ratio varying from 1 to 0.9 (back to front).

Se within the precursors

The composition now shows a more uniform Se content. This suggests that this precursor scheme can be used to tune the S/(S+Se) ratio, and variations from 1 to 0.5 were achieved. Custom vertical gradients could be possible by tuning the thickness of the Se layer within each precursor period.

Blister Investigation





SEM images of absorbers from the same precursor! Blistering is dependent on the heating rate

$0.5\ ^{\circ}C/s$ $0.2\ ^{\circ}C/s$

Heating Rate

It was found that blister formation is closely related to the heating rate during the annealing step. Very low ($< 0.2^{\circ}C/s$) and very high ($> 5^{\circ}C/s$) heating rates were found to almost eliminate blistering, while intermediate led to severe blistering.

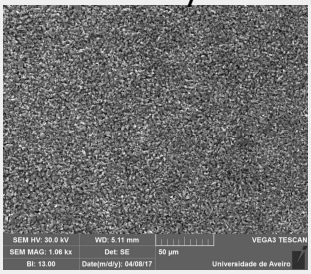
Competing phenomena?

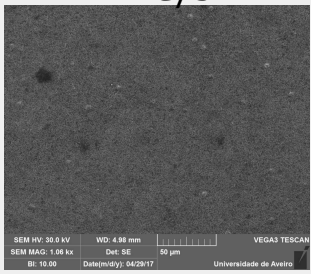
Volatilization Losses VS **CZTS Formation**

A very fast annealing has low volatilization losses, while a very slow annealing hinders blister growth dynamics due to weaker temperature gradients.

No Blisters!

$0.1\ ^{\circ}C/s$ $7\ ^{\circ}C/s$





Conclusion

The Se depth profile hints that a bandgap grading is possible using the proposed precursor configurations.

Blistering was shown to be strongly dependent on the heating rate during annealing, and two different blister-free regions were identified. An explanation based on the competition between volatilization losses and CZTS formation is proposed to explain the results.